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10/634,880	08/06/2003	Tae-Hyun Kim	253/028	7538

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EXAMINER

WEBB, GREGORY E

ART UNIT	PAPER NUMBER
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1751

DATE MAILED: 05/31/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

Office Action Summary

Application No.

10/634,880

Applicant(s)

KIM ET AL.

Examiner

Gregory E. Webb

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-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 08062003.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-19 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 1-19 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☒ All b) ☐ Some * c) ☐ None of:
1. ☒ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)
Paper No(s)/Mail Date 020504,072704.
- 4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____
- 5) ☐ Notice of Informal Patent Application (PTO-152)
- 6) ☐ Other: _____

DETAILED ACTION

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

(e) the invention was described in (1) an application for patent, published under section 122(b), by another filed in the United States before the invention by the applicant for patent or (2) a patent granted on an application for patent by another filed in the United States before the invention by the applicant for patent, except that an international application filed under the treaty defined in section 351(a) shall have the effects for purposes of this subsection of an application filed in the United States only if the international application designated the United States and was published under Article 21(2) of such treaty in the English language.

(e) the invention was described in a patent granted on an application for patent by another filed in the United States before the invention thereof by the applicant for patent, or on an international application by another who has fulfilled the requirements of paragraphs (1), (2), and (4) of section 371(c) of this title before the invention thereof by the applicant for patent.

The changes made to 35 U.S.C. 102(e) by the American Inventors Protection Act of 1999 (AIPA) and the Intellectual Property and High Technology Technical Amendments Act of 2002 do not apply when the reference is a U.S. patent resulting directly or indirectly from an international application filed before November 29, 2000. Therefore, the prior art date of the reference is determined under 35 U.S.C. 102(e) prior to the amendment by the AIPA (pre-AIPA 35 U.S.C. 102(e)).

The applicant's claims are drawn to two types of inventions. The first being a composition containing 1) any hydroxyl containing compound; 2) any fluorine ion containing compound; and an oxidizing agent. The second inventive concept involves methods of using similar compositions for etching a semiconductor substrate.

The applicant teaches various hydroxyl containing compounds with the ammonium hydroxide being preferred. Concerning the fluoride compound, the applicant's claim 7 teaches the preferred use of hydrogen fluoride as this fluoride ion containing compound.

Claims 1-19 are rejected under 35 U.S.C. 102(e) as being anticipated by Lee et al (US 6,391,793).

Concerning the claimed nitric acid, claimed fluoride compound and the preferred fluoride compound, Lee teaches the following:

Wafers were etched in a hydrofluoric acid and nitric acid composition including about 1% by volume of hydrofluoric acid and about 99% by volume of nitric acid. The selectivity between silicon and thermal oxide was less than 1.(see example 1)

Concerning the claimed pH range, Lee teaches the preferred pH range of 7 to about 8 (see claim 1).

Concerning the claimed oxidizing agent, Lee teaches the following:

The oxidizing agent of the etch composition may be any oxidizing agent such as hydrogen peroxide or ozone. Preferably, the oxidizing agent is hydrogen peroxide.(see cols. 4-5)

Concerning the preferred acid, Lee teaches the following:

Wafers were etched in a polysilicon etch composition including 2% hydrofluoric acid, 40% nitric acid, and 58% acetic acid. The selectivity

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between silicon and thermal oxide was less than 1.(see example 2)

Concerning the preferred hydroxide compound, Lee teaches the following:

The above ranges for the etch composition are particularly applicable to the use of ammonium fluoride and hydrogen peroxide but appear to be equally applicable to etch compositions having other combinations of components as described above, such as when ammonium fluoride is provided by ammonium hydroxide and hydrofluoric acid. In other words, suitable amounts of ammonium hydroxide and hydrofluoric acid may be mixed to provide an adequate amount of ammonium fluoride. When ozone is used as the oxidizing agent, ozone is preferably present in a range of about 1 parts per million (ppm) to about 5 ppm.(see col. 5, lines lines 38-48)

Concerning the claimed dry etching step, Lee teaches the following:

After definition of the trench 21, a thermal oxide layer 22 may be formed on the walls of the trench, e.g., sidewalls and bottom surface. An oxide is then formed to fill the trench 21 to a height at least as great as the silicon nitride/pad oxide stack used for defining the trench 21.

Generally, the oxide material 24 is a high density plasma (HDP) oxide material.(see col. 7, lines 42-47)

Claims 1-19 are rejected under 35 U.S.C. 102(e) as being anticipated by Chen (US6794307).

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Concerning the claimed intended use, Chen teaches the following:

As shown in FIG. 4, after formation of the contact opening 31 the photoresist layer may be stripped using available methods. Removal of the photoresist layer leaves the exposed DARC layer 27 over the second insulative layer 25 which must also be removed. The DARC layer 27, comprised of silicon oxynitride, and although a solid dielectric layer it has a tendency to leak at times, and may therefore interfere with subsequent metallization of the contact opening 31, e.g. metallization during capacitor formation. Its removal is therefore highly desirable. At the same, it is also desirable to remove this layer with minimal effect on the second insulating layer 25, e.g. with minimal or no removal of layer 25.(see col. 2, lines 1-13)

Concerning the claimed nitric acid and hydrogen peroxide, Chen teaches the following:

7. The method of claim 6, wherein said oxidizing agent is at least one member selected from the group consisting of hydrogen peroxide (H.sub.2O.sub.2), ozone (O.sub.3), ammonium persulfate and nitric acid.(see claim 7)

Concerning the claimed pH range, Chen teaches the following:

In another embodiment of the invention, the removal mixture may have a pH within the range of about 4 to about 14, and desirably may have a substantially neutral pH which is within the range of about 6.5 to about 8.5. More preferably, the pH of the solution is within the range of about 7 to about 8, and is more preferably about 7. Etch rate selectivities as

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described above can still be obtained within these pH ranges, with the additional advantage being that the removal mixture is not overly caustic or corrosive.(see col. 5, lines 57-65)

Concerning the claimed oxidizing agent, Chen teaches the following:

8. The method of claim 7, wherein said oxidizing agent is hydrogen peroxide (H.sub.2 O.sub.2).(see claim 8)

Concerning the claimed fluoride compound, preferred fluoride compound and the preferred hydroxide compound, Chen teaches the following:

17. The method of claim 16, wherein said method further comprises generating said tetramethylammonium fluoride from a reaction mixture of tetramethylammonium hydroxide and hydrofluoric acid.(see claim 17)

Concerning the preferred acid, Chen teaches the following:

contacting said coating layer with a removal mixture comprising tetramethylammonium fluoride and at least one acid selected from the group consisting of hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, acetic acid, citric acid, sulfuric acid, carbonic acid and ethylenediamine tetraacetic acid, said contacting being sufficient to remove said coating layer.(see claim 20)

Concerning the claimed dry etch and ashing step, Chen teaches the following:

Another application of the invention is shown with respect to FIG. 10. A semiconductor device 210 in an intermediate stage of fabrication has an opening 216 formed in an insulative layer 214 which in turn has been

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formed over a substrate 212. The substrate is comprised of silicon, or silicon-on-insulator material as previously described with reference to FIG. 1. A layer of native oxide 218 has been deposited in the opening 216 over the substrate 212 using available materials and techniques.

Subsequent removal of the native oxide layer 218 is desirable as part of a pre-diffusion cleaning step. In this process, the native oxide layer 218 is removed from the substrate so that dopants may then be diffused into the substrate to form an active, doped region as illustrated by the line 220. Use of the removal mixture of the invention as heretofore described will effectively remove the native oxide 118 while not corroding either the insulative layer 214 or the substrate 212.(see cols. 7-8)

Claims 1-19 are rejected under 35 U.S.C. 102(b) as being anticipated by Somers (US4410396).

Concerning the claimed intended use, Somers teaches the following:

The solder stripping properties of a chemical stripping solution in accordance with the present invention was compared with Solution A as set out in Example 4, above. A resin printed circuitboard carrying a copper layer 40 microns thick with a layer of solder 20 microns thick was immersed in a quantity of Solution A. Under moderate magnetic agitation, no marked stripping of solder was observed. Secondly, a printed

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circuitboard was subjected to the spray treatment as described in Example 1 except that Solution A was used instead of the solution of Example 1. A stripping rate of 0.7 um/min was observed as compared to a stripping rate of 14 um/min when the solution of Example 1 was used.(see example 5)

Concerning the claimed hydrogen peroxide, the pH and the claimed oxidizing agent, Somers teaches in claim 1 a composition containing ammonium fluoride (a combination of ammonium hydroxide and hydrogen fluoride; see below).

Concerning the claimed pH range, Somers teaches the following:

In accordance with the present invention, one has to make certain that the pH at the surface being stripped remains below that at which smut formation occurs (5.3 in the case of copper). Thus the presence of hydrogen peroxide in the stripping reaction causes the pH to tend to rise during stripping as compared with the pH of the bulk solution and therefore one needs to make certain that the initial pH of the bulk solution is at such level that in use the pH at the surface will not rise above the critical pH value. For copper it has been found that an initial pH of not more than 4.0 produces an effective system in which smut formation is avoided.(see col. 6, lines 28-38)

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Concerning the claimed fluoride compound, preferred fluoride compound and the preferred hydroxide compound, Somers teaches the following:

Ammonium bifluoride is the preferred commercially available source of hydrofluoric acid but other reactive compositions of ammonia with hydrofluoric acid or salts thereof, such as ammonium fluoride, have also proved effective and their use is equally contemplated within the scope of the present invention. It would appear that the hydrofluoric acid is the active component and the ammonia appears to have some inhibiting function on the hydrofluoric acid in reducing or preventing its attack on the copper. Such other ammonia/hydrofluoric acid salts or mixtures, in addition to ammonium fluoride, which may be used, include mixtures of ammonium halides with hydrofluoric acid.(see col. 4, lines 39-51)

Concerning the preferred acid, Somers teaches the following:

Pursuant to the above objects, it has now been found that a solder stripping composition, having significantly increased stripping rates and reduced attack on the substrate, can be formulated with hydrogen peroxide, ammonium fluoride or bifluoride, an acid and an 8-hydroxyquinoline compound by utilizing these components in certain specific amounts while maintaining certain specific ratios of these components to each other. The improved solder stripping composition of the present invention is an aqueous solution containing hydrogen peroxide (Component A) in an amount of about 0.1 to about 10 molar, ammonium fluoride or ammonium bifluoride

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(Component B) in an amount of from about 0.4 to about 10 molar, an inorganic acid (Component C) in an amount at least sufficient to maintain the pH of the solution at the surface being stripped below the value at which smut formation occurs and, as a metal complexing compound, an 8-hydroxyquinoline compound (Component D) in an amount of at least about 0.005 molar. Additionally, in the composition of the present invention, the molar ratio of hydrogen ions to Component D is at least 100:1, and desirably the molar ratio of Component A to Component B is at most 1:1, e.g. at most 0.91:1. It is also desirable that the molar ratio of the ammonium fluoride or bifluoride (B) to the metal complexing compound (D) will be at least 125:1 and the molar ratio of the hydrogen peroxide (A) to the metal complexing compound (D) will be at least 50:1. When this composition is used, in either a spray or immersion process, and particularly, when it is used with sulfuric acid as a preferred acid in an amount sufficient to maintain the bath pH at a value which is not in excess of about 5.3 and is further used with a weight ratio of ammonium bifluoride or fluoride (calculated as ammonium bifluoride) to hydrogen peroxide which is in excess of about 1.25:1, very rapid stripping of tin and tin/lead solders from metal substrates, such as copper, is obtained without significant attack of the copper substrate. (see cols. 2-3)

Claims 1-19 are rejected under 35 U.S.C. 102(b) as being anticipated by Verhaverbeke (US6132522).

Concerning the claimed intended use, Verhaverbeke teaches the following:

The invention presents, inter alia, wet processing methods useful in the manufacture of electronic component precursors, such as semiconductor wafers and flat panels, used in integrated circuits. These novel methods can be used for the cleaning, stripping, and/or etching of such electronic component precursors.(see col. 1, lines 5-15)

Concerning the claimed nitric acid, Verhaverbeke teaches the following:

Similarly, the present invention may be used with chemical reagents to remove photoresist material from electronic component precursors. Process fluids suitable for these treatments include, without limitation, solutions of sulfuric acid with ozone; sulfuric acid and ozone and/or hydrogen peroxide; inorganic acids such as sulfuric acid, nitric acid, chromic acid, and phosphoric acid; and hydrogen peroxide. Sulfuric/chromic and sulfuric/nitric are typically used at 100.degree. C. Fuming nitric acid, also still in use today, is typically used at room temperature.

Preferred process fluids are solutions of sulfuric acid and hydrogen peroxide (referred to as Piranha) and sulfuric acid and ozone (referred to as SOM: Sulfuric Ozone Mixture).(see cols. 6-7)

Concerning the claimed pH range, Verhaverbeke teaches the following:

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Generally, after the wafers are treated with the first basic process fluid (as discussed above) or any other process fluid, a DI rinse is typically done to remove the chemicals from the surfaces of the wafers. Because the DI rinse tends to decrease the pH of the resultant solution (discussed above), which in turn decreases the solubility of the silica, precipitation of silica generally occurs with rinsing (due to the co-precipitation of silica and metal precipitates in the chemical solution), with the metal ions acting to "seed" this precipitation reaction. The materials thought to be most responsible for the precipitation in the ammonium hydroxide/hydrogen peroxide process fluid are Fe, Al, and Zn. Other precipitate forming metals in this solution are Pb, Cu, Ni, Hg, and Cr. These metals are trace contaminants in chemicals used in electronic component precursor wet processing. (see col. 2, lines 29-44)

Concerning the claimed oxidizing agent and the preferred hydroxide compound, Verhaverbeke teaches the following:

14. The method of claim 13 wherein the first and second carrier liquids comprise deionized water, the first chemical is selected from the group consisting of hydrochloric acid, ammonium hydroxide, hydrogen peroxide, sulfuric acid, mixtures of sulfuric acid and ozone, mixtures of sulfuric acid and hydrogen peroxide, mixtures of hydrogen peroxide and ammonium hydroxide, and mixtures of hydrogen peroxide and hydrochloric acid, and the second chemical is selected from the group consisting hydrochloric

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acid, ammonium hydroxide, hydrogen peroxide, sulfuric acid, hydrofluoric acid, buffered hydrofluoric acid, mixtures of sulfuric acid and ozone, mixtures of hydrogen peroxide and ammonium hydroxide, and mixtures of hydrogen peroxide and hydrochloric acid.(see claim 14)

Concerning the claimed fluoride compound, preferred fluoride compound and the claimed ashing step, Verhaverbeke teaches the following:

For example, the methods of the invention may be used for etching the surfaces of semiconductor wafers to remove any unwanted oxide layer from the silicon surface. The present invention may also be used in controlled oxide etching. Typical etchants for silicon dioxide include, without limitation, hydrofluoric acid, or ammonium fluoride buffered hydrofluoric acid.(see col. 6, lines 52-60)

Concerning the preferred acid, Verhaverbeke teaches the following:

b) providing a volume of a first reactive process liquid to the reaction chamber, wherein the first reactive process liquid comprises at least one first chemical, and wherein the first chemical has a concentration greater than 100 ppm in the first reactive process liquid and is selected from the group consisting of hydrochloric acid and buffers comprising the same, ammonium hydroxide and buffers comprising the same, hydrogen peroxide, sulfuric acid and buffers comprising the same, mixtures of sulfuric acid and ozone, hydrofluoric acid and buffers comprising the same, chromic acid and buffers comprising the same, phosphoric acid and buffers comprising

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the same, acetic acid and buffers comprising the same, nitric acid and buffers comprising the same, and combinations thereof,(see claim 1)

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Gregory E. Webb whose telephone number is 571-272-1325. The examiner can normally be reached on 9:00-17:30 (m-f).

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Yogendra Gupta can be reached on 571-272-1316. The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).



Gregory E. Webb
Primary Examiner
Art Unit 1751

gew